A Novel Autonomous Process Chain for Selective Precipitation of $CaCO_3$ and $MgCO_3$ using Extracted Mine Tailings

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1. Motivation

- Carbon capture, utilization and storage (CCUS) is an effective approach for the removal of already-emitted CO_2.
- Mine tailings and wastes, rich in Calcium and Magnesium, are used as sources for Carbonation.

Goal: The primary objective of the project is to:

- ❑ Selective precipitation of high-purity $CaCO_3$ and $MgCO_3$ with defined particle size.
- ❑ Develop an autonomous, self-learning process chain for the creation of Self-Learning Robust Autonomous Controller (SLARC).

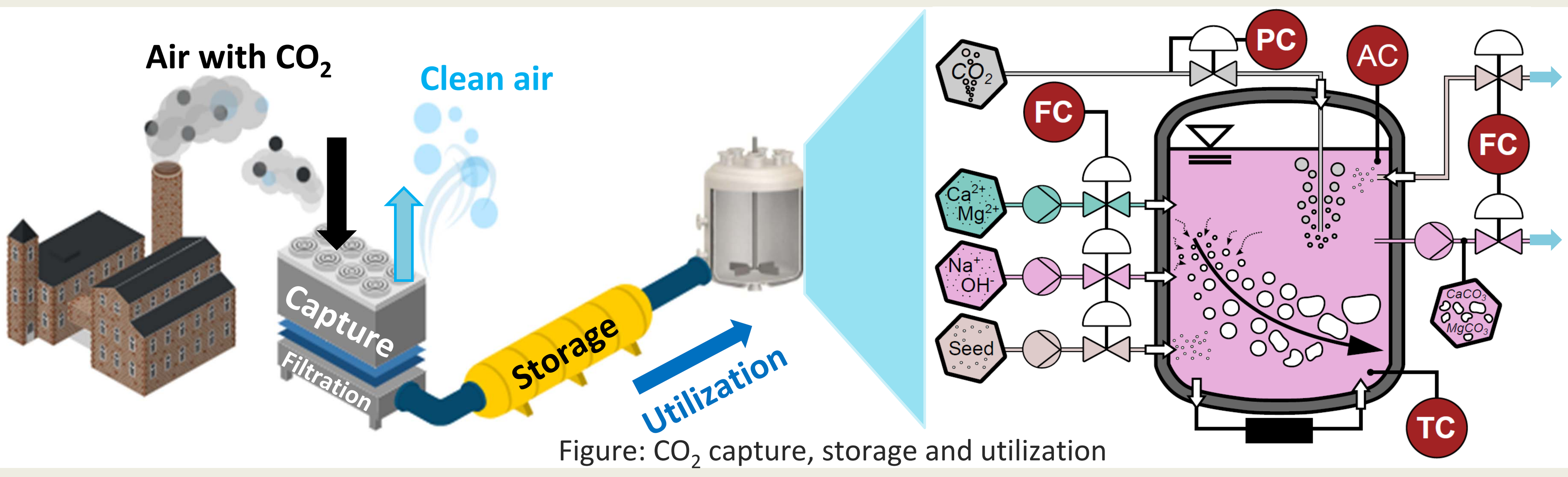


Figure: CO_2 capture, storage and utilization

2. Methodology

- pH swing process used to achieve indirect carbon capture.
- Ca^{2+} and Mg^{2+} extracted at low pH conditions.
- Carbonate precipitation preferred at higher pH values.

Carbonate precipitation

- Extracted Ca^{2+} and Mg^{2+} from the mine tailings are carbonated as –

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \overset{K_{sp,CaCO_3}}{\rightleftharpoons} CaCO_3(aq)$$

$$Mg^{2+}(aq) + CO_3^{2-}(aq) \overset{K_{sp,MgCO_3}}{\rightleftharpoons} MgCO_3(aq)$$

- Solubility product (K_{sp}) and Supersaturation (S) pH dependency is –

$$K_{sp} = [Cat]_{sat}[CO_3^{2-}]$$

$$S = \sqrt{[Cat][CO_3^{2-}]} - \sqrt{K_{sp}}$$

$$[Cat] = Ca^{2+} / Mg^{2+}$$

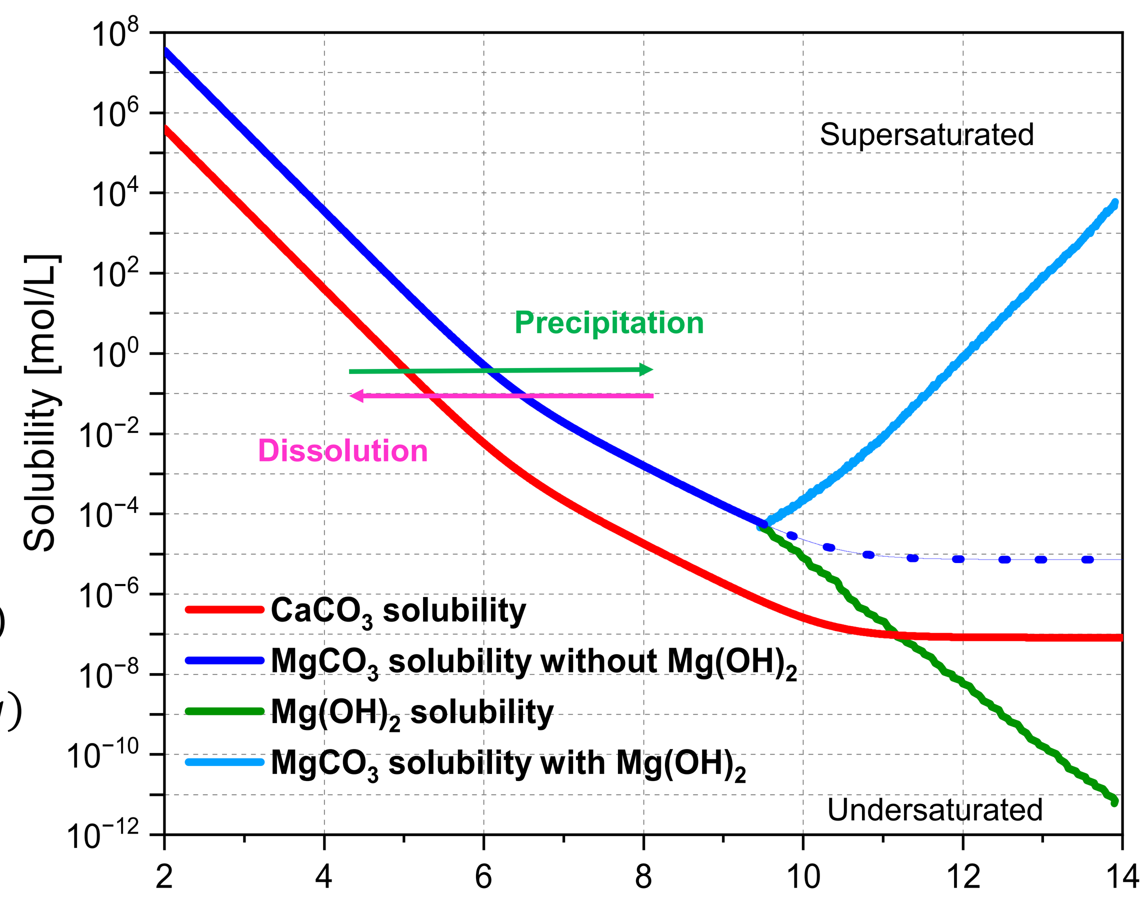
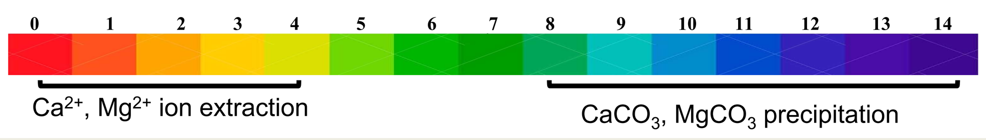


Figure: Solubility curve for $CaCO_3$ and $MgCO_3$



3. Model Development

Semi-Batch Process Model

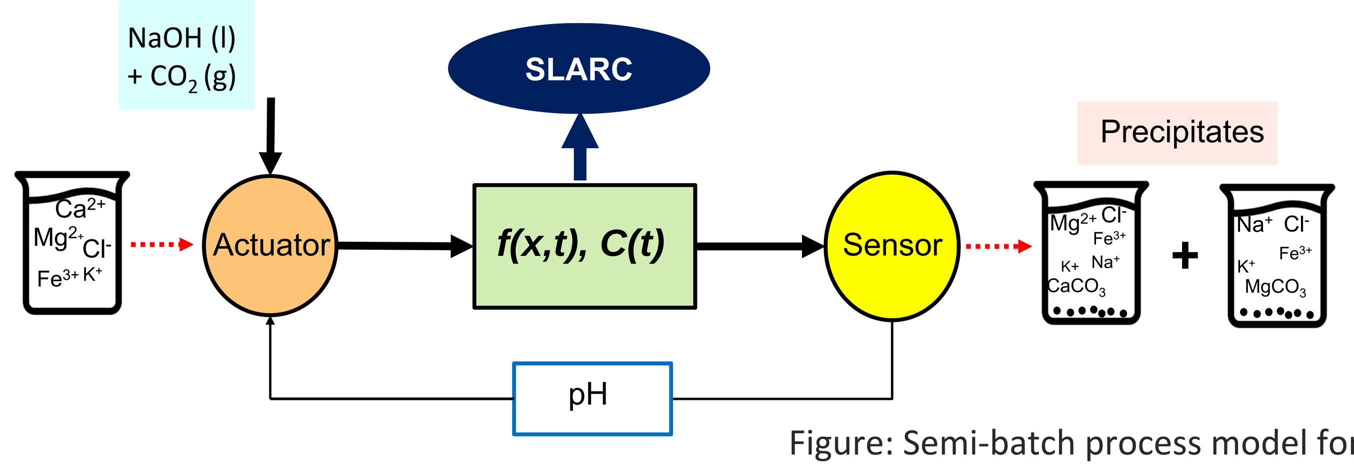


Figure: Semi-batch process model for Selective Precipitation

Population balance equation –

$$\frac{\partial f(t,x)}{\partial t} + G(t)\frac{\partial f(t,x)}{\partial x} = B(t) - D(t)$$

IC & BC:

$$f(x, t = 0) = f_{seeds}(x)$$
$$f(x = 0, t) = 0$$

Change in concentration for $CaCO_3$ in aqueous state –

$$V(t)\frac{dC(t)}{dt} = V(t)r(t) - \dot{V}_{in}C(t) - \rho^m k_v G(t) m_2(t) - \rho^m v_{nuc}[B(t) - D(t)]$$

IC $C(t = 0) = 0$

where, Growth rate: $G(t) = k_g(S)^g$

Birth rate: $B(t) = k_B(S)^B$ Death rate $D(t) = k_d(S)^d$

Reaction rate: $r(t) = [Ca^{2+}][CO_3^{2-}]$

4. Experimental Investigation

pH-swing process for Selective precipitation of $CaCO_3$ and $MgCO_3$

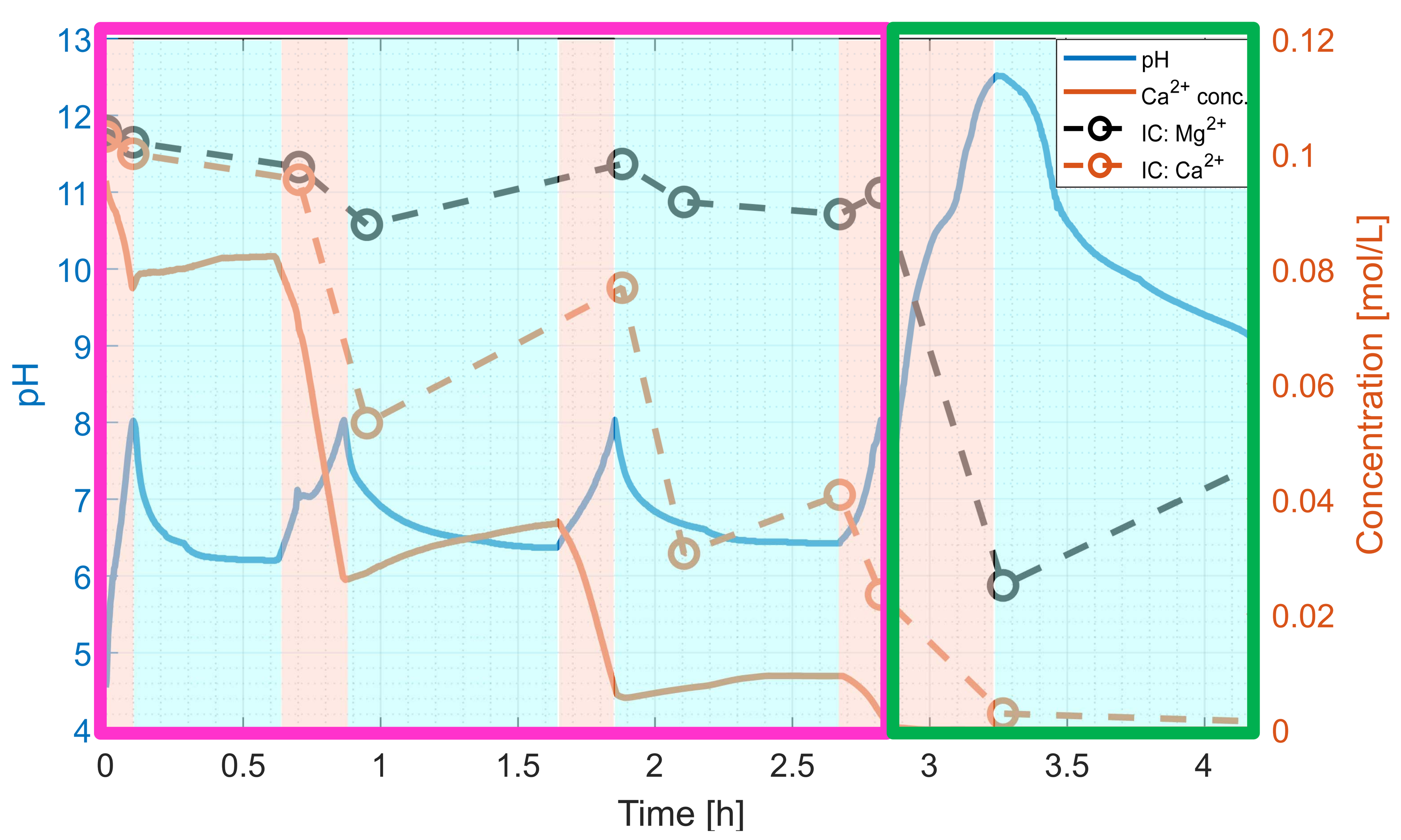


Figure: Selective precipitation of $CaCO_3$ and $MgCO_3$ by alternate addition of CO_2 and NaOH

NaOH (l) addition – pH increase	CO_2 (g) addition – pH decrease

- pH shifted by alternative addition of CO_2 and NaOH.
- $CaCO_3$ and $MgCO_3$ precipitated selectively one after another.

$CaCO_3$ precipitation

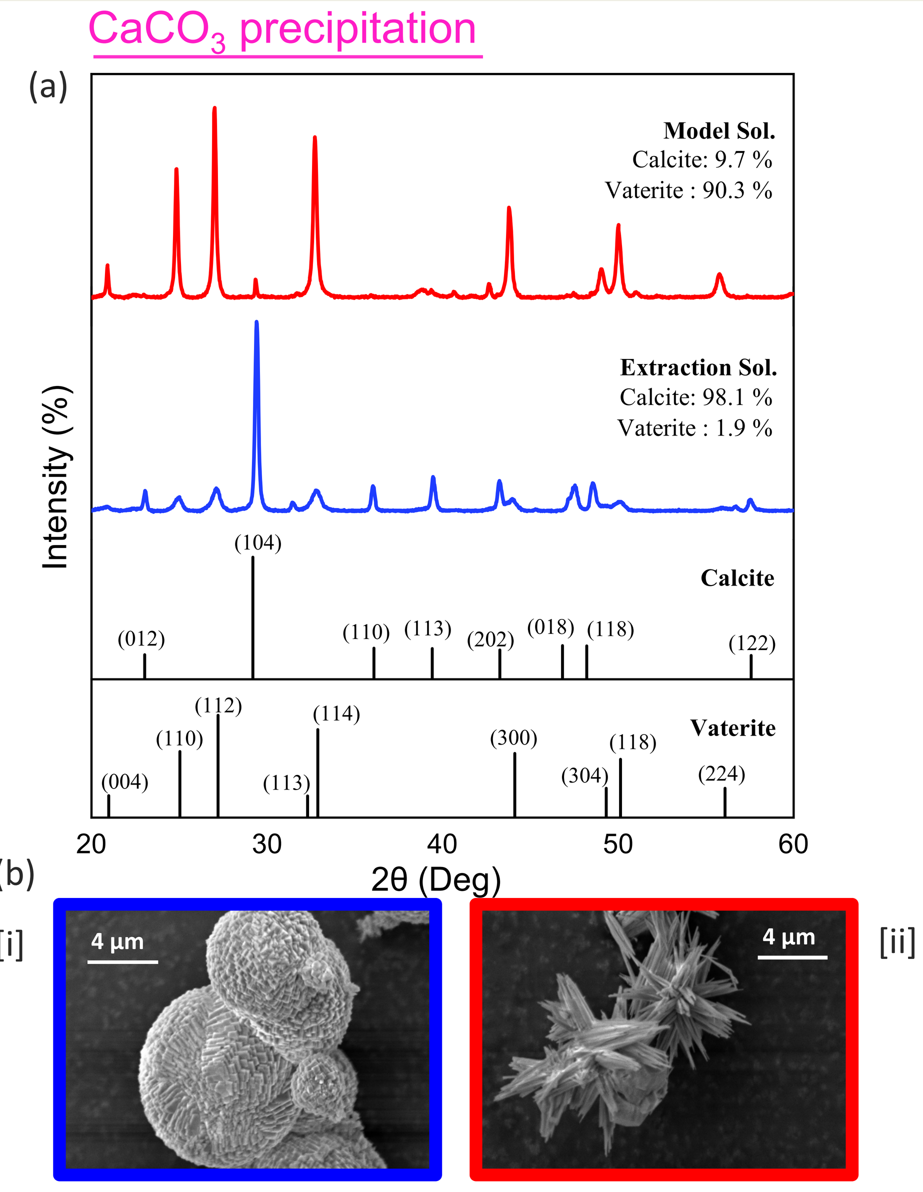


Figure: (a) XRD analysis of model and extraction solution

(b) SEM image: [i] Calcite (extraction sol.) [ii] Vaterite (model sol.)

$MgCO_3$ precipitation

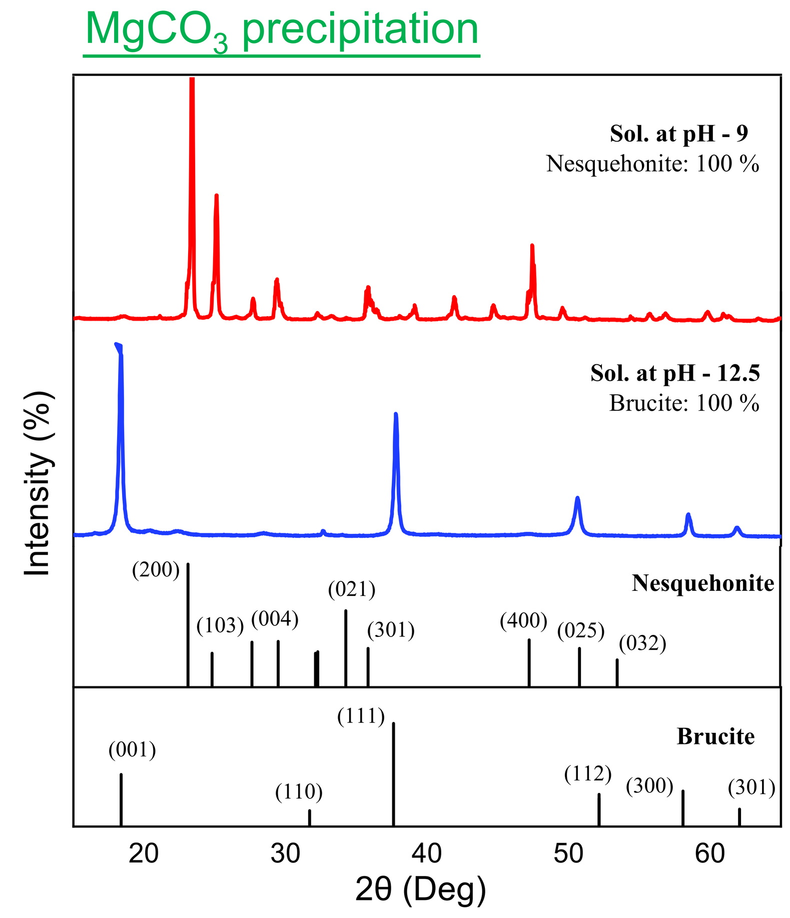


Figure: XRD analysis of Nesquehonite precipitation via intermediate Brucite

pH = 12.5 ⟶

$$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$$ (Brucite)

pH = 9 ⟶

$$Mg(OH)_2(s) \overset{CO_2}{\Longrightarrow} MgCO_3.3H_2O(s)$$ (Nesquehonite)

Future Endeavors

- Complete model development for the autonomous control of selective precipitation.
- Model parameter estimation for control of crystal morphology and particle size distribution.
- Further optimization of the selective precipitation process to maximize the product output.
- Close the mass balance loop by incorporating the recycling of the acids and bases used.

References

[1] C. Hegde, A. Voigt, and K. Sundmacher, "Towards pH Swing-based CO2 Mineralization by Calcium Carbonate Precipitation: Modeling and Experimental Analysis," in Proceedings of the 34th European Symposium on Computer Aided Process Engineering (ESCAPE34/PSE24), Florence: Elsevier B.V., Jun. 2024, pp. 1519–1524.

[2] S. Hiremath, M. Kakanov, A. Voigt, K. Sundmacher, and N. Bajcinca, "Learning-based Adaptive Robust Control of a Precipitation Process," in Proceedings of the 34th European Symposium on Computer Aided Process Engineering (ESCAPE34/PSE24), Florence: Elsevier B.V., Jun. 2024, pp. 1801–1806.

3. Acknowledgement

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See also: Presentation by **Chinmay Hegde – Friday,13.07.2024 at 11:30 am, Graf-Soden-Zimmer**

"Development of an autonomous process for the selective extraction and precipitation of carbonates from mining waste"